

A Novel Proton Sensor with Luminescence and Color Signaling Based on Platinum(II) Terpyridyl Acetylide Complex

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A novel sensitive probe for proton based on platinum(II) terpyridyl acetylide complex by monitoring the changes both in luminescence and color is described.

Keywords proton sensor, platinum(II) terpyridyl complex, acetylide, luminescence, LLCT (ligand-to-ligand charge transfer), MLCT (metal-to-ligand charge transfer)

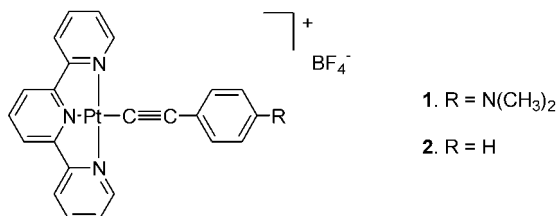
Molecular switches that are controllable, reversible and readable at molecular level are an essential component of molecular electronics¹ and chemical sensors.²⁻⁶ Of particular interest are the molecules which show dramatic and reversible changes in color and/or luminescence in visible spectral region upon exposure to specific substrates. A number of “chromophore-spacer-receptor” systems that can selectively recognize specific guest molecules at their receptor site and produce measurable color and/or luminescence changes have been described.²⁻⁶ Up to now most of such systems are based on organic chromophores,^{2,3} although there has been increasing attention given to the design of metalloreceptors in recent years.⁴⁻⁶ Among the relatively few metalloreceptor examples, systems with metal-to-ligand charge transfer (MLCT) excited states are known,^{4,5} while reports on other systems are rare.⁶ Here we describe the use of the platinum(II) terpyridyl acetylide complex containing a simple amine group in the acetylide ligand (Chart 1, Complex **1**) as a sensitive probe for detection of protons. In neutral or basic solution complex **1** is non-emissive and its low energy absorption mainly arises from ligand-to-ligand charge transfer (LLCT) transition. Upon protonation, this

complex displays bright luminescence and its MLCT transition becomes the lowest energy absorption. Thus, complex **1** can be utilized as a chemosensor for detection of protons by monitoring the changes both in luminescence and color.

Complex **1** was prepared by the reaction of [Pt(trpy)Cl]Cl (trpy = 2,2':6',2''-terpyridine) with 2 equivalent amounts of *p*-[(*N,N*-dimethyl)amino]phenylacetylide in DMF in the presence of catalyst CuI and triethylamine at room temperature.⁷ After metathesis reaction by KBF₄ and recrystallization of the crude product by vapor diffusion of diethyl ether into an acetonitrile solution, **1** was obtained as dark blue crystals with *ca.* 80% yield. The identity of this complex was confirmed by ¹H NMR spectroscopy, MS spectrometry and satisfactory elemental analyses.⁸ For comparison, complex **2**, [Pt(trpy)(C≡CPh)]BF₄, was also synthesized by a similar procedure.

Figure 1 presents the changes in the UV-vis spectrum of **1** as a function of added acid concentration. This complex in neutral acetonitrile solution is deep purple and exhibits intense vibronic-structured absorption bands at $\lambda < 350$ nm with extinction coefficients (ϵ) on the order of $10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, and a less intense band at 380—450 nm (centered at *ca.* 410 nm, $\epsilon = 2860 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). Significantly, a moderately intense low-energy absorption in the region of 460—650 nm (absorption maximum $\lambda_{\text{max}} = 535 \text{ nm}$, $\epsilon = 4920 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) is observed. The absorption spectral properties are found to follow Beer's Law at concentrations below $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, suggesting that no any significant complex aggregation occurs. With reference to previous spectroscopic work on platinum(II) terpyridyl complexes,^{5a,7a,9} the absorption bands at $\lambda < 350$ nm are assigned to the intraligand (IL) transition of

Chart 1 Structure of complexes **1** and **2**



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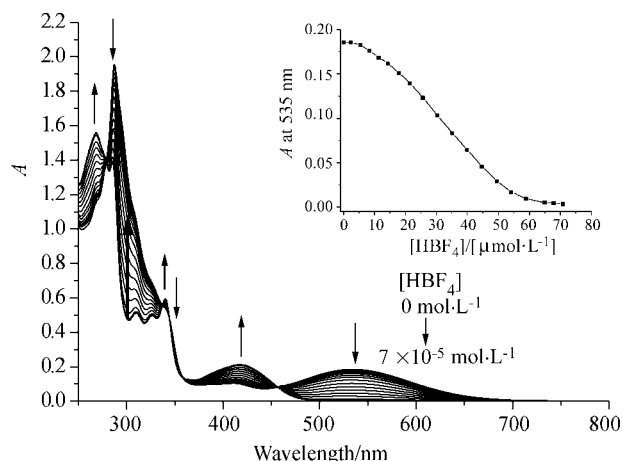


Figure 1 Absorption spectral of **1** ($3.87 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) upon addition of various concentrations (0 – $7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) of HBF_4 in acetonitrile. The insert shows the plot of the absorbance at 535 nm vs. concentration of HBF_4 .

terpyridyl and acetylide ligands as well as the charge transfer transition involved in the $\text{Pt}-\text{C}\equiv\text{CPh}$ moiety, while the absorption band at 380–450 nm is ascribed to the $d\pi(\text{Pt}) \rightarrow \pi^*(\text{trpy})$ MLCT transition. The low-energy absorption band at 535 nm is tentatively assigned to the LLCT transition from the amine-substituted acetylide ligand to the terpyridyl acceptor. This assignment is based upon the following observations. First, the energy of the band increases with solvent polarity. For example, the λ_{max} of the band is blue-shifted from 595 nm in dichloromethane to 535 nm in acetonitrile, which supports the charge transfer assignment. Second, we have performed cyclic voltammetry studies on complexes **1** and **2** in acetonitrile. Both complexes exhibit two quasi-reversible cathodic waves in the potential region of -0.8 to -1.5 V vs. SCE, which were ascribed to the reduction of the terpyridyl ligand with some mixing of the Pt(II) character^{5a,7a}. Complex **2** displays an irreversible anodic wave with E_p at $+1.22$ V vs. SCE. This wave has been assigned to the metal-center oxidation from Pt(II) to Pt(III) by Yam and coworkers.^{5a} We could not detect the oxidation wave for the Pt(II) site in **1**. The undetectable oxidation wave is preceded for certain platinum(II) complex¹⁰. However, we observed an irreversible anodic wave near $+0.63$ V vs. SCE. Upon addition of an acid to the solution, this wave disappeared. We assigned this wave to the oxidation of the amine-substituted acetylide ligand. Cyclic voltammetry of uncomplexed ligand, *p*-[(*N,N*-dimethyl)amino]phenylacetylide, exhibits a similar anodic wave at a slightly more positive potential (*ca.* $+0.85$ V vs. SCE). Obviously, the LLCT transition in **1** should be in the lower energy than the MLCT transition. Third, upon addition of HBF_4 to the solution in acetonitrile **1** becomes yellow. The low-energy band at 535 nm decreases monotonically throughout the addition and completely disappears toward the end of the titration, while the absorption band at 410 nm concomitantly

grows with increasing HBF_4 concentration. Isosbestic points are observed at 457, 358, 344, 337 and 279 nm. The insert in Figure 1 shows the absorbance at 535 nm as a function of the concentration of added HBF_4 . This observation is evidently attributed to the protonation of the amine group in the acetylide ligand. As the amine receptor was protonated in the presence of HBF_4 , the LLCT transition shifted to much higher energy and $d\pi(\text{Pt}) \rightarrow \pi^*(\text{trpy})$ MLCT became the lowest-lying excited state. In control experiment with complex **2**, the addition of HBF_4 did not have a marked effect on the absorption spectrum. Taking the above observations together, the absorption band at 535 nm is consistent with the assignment of an LLCT transition. The LLCT excited states have been well preceded for platinum(II) diimine complexes.¹¹

The change in the luminescence response of complex **1** towards proton was found to be even more pronounced. In neutral or basic solution **1** is non-emissive. The lack of emission, when the LLCT band is excited, is probably due to the facile non-radiative deactivation of the low-lying LLCT excited state. However, in acidic media **1** exhibits a structureless emission band centered at *ca.* 560 nm. Figure 2 shows the changes in the emission spectrum of **1** as a function of HBF_4 concentration. Throughout the titration, the excitation wavelength corresponds to the isosbestic point found at 457 nm in Figure 1. The emission intensity is noticeably enhanced upon increasing HBF_4 concentration with saturation observed toward the end of the titration, while the shape and energy of the emission band remain no variations. With reference to the previous work on the emission of platinum(II) terpyridyl complexes,^{5a,7a,9} this emission is assigned as derived from the $d\pi(\text{Pt}) \rightarrow \pi^*(\text{trpy})$ MLCT excited state. The insert in Figure 2 shows the plot of the emission intensity at 560 nm against the concentration

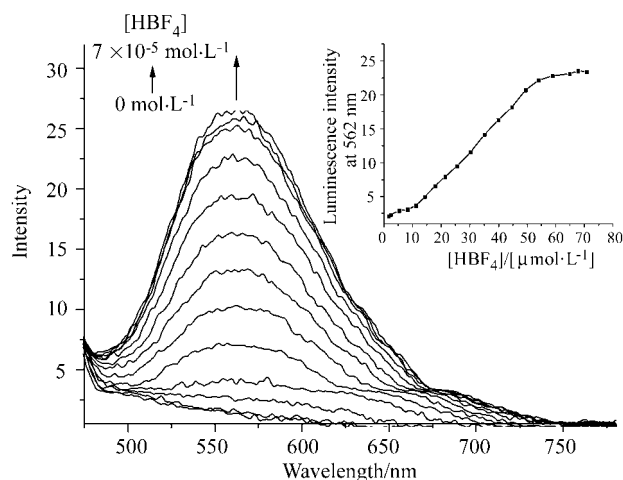


Figure 2 Luminescence spectral changes of **1** ($3.87 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) upon addition of various concentrations (0 – $7 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) of HBF_4 in acetonitrile. The insert shows the luminescence intensity at 560 nm as a function of HBF_4 concentration.

of HBF_4 . The emission quantum yield and lifetime of **1** in its protonated form were measured to be 0.001 and 0.02 μs respectively.¹² Similar to the absorption studies, control experiments with complex **2** under the same conditions showed no change in the emission characteristics upon addition of HBF_4 . More interestingly, the changes in absorption and emission behavior for complex **1** are fully reversible. Successive addition of a base (e.g. triethylamine) to the acidic solution of **1** in acetonitrile led to the observation of a reverse trend; the luminescence was gradually quenched, and the absorbance at 410 nm dropped with a concomitant rise in the absorption at 535 nm. Eventually the LLCT band in the absorption spectrum was totally recovered, and the solution became deep purple. This result is indicative of the reversible nature of the protonation and deprotonation processes for the amine group in complex **1**.

In summary, we have synthesized a chemosensor for detection of protons in micromolar concentration by monitoring the changes in luminescence and color. Our future efforts will be focused on developing chemosensors for detection of metal ions by appending versatile molecular recognition units to the current molecular design.

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- Complex **1**: $^1\text{H NMR}$ ($\text{DMSO}-d_6$): 2.93 (s, 6H), 6.68 (d, $J=8.4$ Hz, 2H), 7.34 (d, $J=8.2$ Hz, 2H), 7.95 (t, $J=6.3$ Hz, 2H), 8.48–8.68 (m, 7H), 9.21 (d, $J=5.1$ Hz, 2H); IR ν : 2115 cm^{-1} . FAB-MS (m/z): 572 (M^+). Anal. calcd for $\text{C}_{25}\text{H}_{21}\text{BF}_4\text{N}_4\text{Pt} \cdot 0.5\text{H}_2\text{O}$: C 44.92, H 3.29, N 8.39; found C 44.87, H 3.59, N 8.58.
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- The lifetime of **1** (4.62×10^{-5} mol \cdot L $^{-1}$) in the presence of excess HBF_4 in degassed acetonitrile solution was determined by a conventional laser system. The excitation source was 355 nm output (third harmonic, 10 ns of pulsed Nd:YAG laser 10 Hz). The quantum yield was obtained by the optical dilute method using a degassed acetonitrile solution of $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ as a reference ($\Phi=0.062$)⁷.